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COMPLETE SPECIFICATION

Improvements in Oriented Melt Span Polyester Filaments

We, E. I. Du Pont De Nemours and Company, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which is it to be performed, to be particularly described in and by the following statement: —

This invention relates to novel oriented, synthetic melt-spun filaments and fibres having reduced static propensity. (Where the context permits, the word "fibres" will be used hereinafter to denote both continuous filaments and fibres of relatively short length, e.g. staple fibre.)

The advent of fibres from wholly synthetic polyesters has made possible textiles having a high level of durability, strength, wash-and-wear properties, and chemical inertness, combined with good aesthetics. However, these fibres are especially prone to develop a static electric charge under conditions of low humidity, which is objectionable during processing, and also in use, especially in wearing apparel and rugs, etc.

In attempts to avoid this difficulty, surface treatments to form on the fibres hydrophilic coatings, primarily polymeric, have been proposed. None of these coatings seem to have been entirely satisfactory, since many have lacked durability, and those sufficiently insolubilised on the fibres to be durable have produced fabrics with a harsh, unattractive hand.

Another approach to an antistatic fibre is to employ a copolymer. Hydrophilic monomers are combined in the polymer chain by copolymerising with a major proportion of hydrophobic monomer. Although in some cases acceptable copolymer compositions have been discovered, these were obtained at the expense of impaired physical properties such as tenacity, elongation, stiffness, durability, wash-wear properties, alkali resistance, and the like.

The present invention comprises textile fibres prepared from melt-spinnable synthetic linear fibre-forming polyester polymers having uniformly admixed therein at least 2% by weight of a high molecular weight poly(alkylene ether). The poly(alkylene ether) is distributed through the filament structure in the form of microscopic elongated particles which are oriented with their longest dimension parallel to the major axis of the filament, giving the fibre a striated appearance.

The poly(alkylene ethers) which may be incorporated in the hydrophobic polymers are condensation products of ethylene oxide, propylene oxide or both; such compounds contain two or three carbon atoms in the alkyl group, being intralinear carbon atoms connecting intralinear ether-oxygen atoms. Preferably, the poly(alkylene ether) is an ethylene oxide polymer which is terminated by no more than one hydroxyl group, and by one or more ether end groups of the formula —OR, where R is an alkyl, aryl, or aralkyl group, as for example methyl, ethyl, i-octyl, decyl, lauryl, tridecyl, nonylphenyl, dodecylphenyl, phenyl and naphthyl. Residues of coupling compounds or chain-initiating agents, for example bisphenol, may be present.

The disadvantage which can arise from the presence in the poly(alkylene ether) of groups which are reactive with the polyester will be readily apparent, since durability, molecular weight, and other physical properties of the hydrophobic polymer are adversely affected by copolymerisation with a poly(alkylene ether). Therefore singly and especially doubly capped polyalkylene oxides are preferred; these should have at least about 30 ethylene oxide units in the chain, corresponding to an average molecular weight (for the polyether portion of a polyethylene oxide), of at least 1300. Higher molecular weights are even more effective, especially about 10,000 to 20,000. (Throughout this specification molecular weight figures are to be taken as the number

average molecular weight.) Especially suitable end groups for these polyethers are nonyl-phenoxy and methoxy radicals. The polyester should contain 3 to 15% of the poly(alkylene ether) to provide a satisfactory level of static protection.

Effective mixing of the poly(alkylene ether) with the polyester is essential in order to distribute the polyether compound sufficiently uniformly throughout the polymer, the blending preferably being carried out at a temperature above the melting point of the polyester. Melting the components in a screw extruder is usually satisfactory, although mechanical mixers are more effective, owing to the high viscosity of the polymer and the poly(alkylene ether).

When the polyether and polyester are melt-blended in a screw melter or other mechanical mixer, and immediately thereafter extruded to form filaments, it will often be possible to use a high molecular weight polyether glycol, since the two components will be in contact in the melt for too short a time for the glycol to become part of the polyester chain, e.g. by ester exchange, to any significant extent. As a guide, reaction with the polyester should be kept to less than 10% of the polyether added in order to avoid harmful effects on the fibre properties. When the special processing conditions described above are employed, if a polyether glycol is used it should have a molecular weight of about 10,000 to 500,000. From 3 to 15% of poly(alkylene ether) is satisfactory to provide washfast static protection.

In order to provide the particulate striated distribution in the polyester, the poly(alkylene ether) must be substantially insoluble therein. In addition, it must be stable under melt spinning conditions suitable for the polyester.

Excessive mixing must be avoided, since this has been found to prevent formation of the two-phase striated structure, giving products which are not antistatic. It is believed that the polyether phase may become so highly dispersed that it no longer serves to conduct away the static charges, or possibly the polyether dissolves in the polyester.

X-ray diagrams of polyethylene terephthalate fibres modified with high molecular weight polyethers show features characteristic of an oriented crystalline polyether glycol phase, and also features characteristic of an oriented crystalline polyethylene terephthalate phase. In contrast, a terephthalate polyester containing polyethylene ether units in the chain, described by D. Coleman in *J. Polymer Sci.*, *14*, 15 (1954), shows no difference between x-ray photographs of the modified polymer containing both polyethylene terephthalate and polyether terephthalate blocks and the unmodified polyethylene terephthalate.

A very sensitive criterion of the adverse effect of so reacting a polyether glycol with a polyester, that the former becomes part of the polymer chain is the effect on the light-fastness of the dyed fibre.

It has been discovered that an unreacted polyether glycol can be extracted substantially completely from polyethylene terephthalate fibres using a solvent which has a swelling effect on the polyester, e.g. methylene chloride. In this way, the extent of reaction can be evaluated; harmful results become serious when more than 10% of the added polyether glycol enters the polyester molecule.

As an example, filaments are spun from a mixture of polyethylene terephthalate and 15% of polyethylene ether glycol of molecular weight 20,000, and are drawn and woven into a filling face satin. A swatch A is extracted with methylene chloride for half an hour, removing about 65% of the added polyether glycol. Swatch A, an untreated swatch B, and a control swatch C containing no polyether glycol are dyed by the same procedure, and are exposed to the ultraviolet light of a Xenon arc. Examination after 40 hours shows equivalent fading of samples A and B, whereas very little fading is noted on control sample C. This indicates that it is not the total amount of polyether glycol which causes the fading, but rather the amount which has become a part of the polymer molecule.

The polyesters to which the invention is applied are the melt spinnable fibre-forming synthetic linear condensation polyesters of bi-functional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain include at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain (*para*-relationship in the case of a single six-membered ring). The polyesters may be derived from any suitable combination of bi-functional ester-forming compounds.

Among the various suitable dicarboxylic acid ester-forming compounds are terephthalic acid, bromoterephthalic acid, 4,4¹-sulphonyl-dibenzoic acid, 4,4¹-diphenic acid, 4,4¹-benzophenone-dicarboxylic acid, 1,2-bis(4-carboxy-phenyl)ethane, 1,2bis(p-carboxyphenoxy)-ethane, bis-4-carboxyphenyl ether and various naphthalenedicarboxylic acids, especially the 1,4-, 1,5, 2,6-, and 2,7- isomers: Isophthalic acid is also suitable, especially when used in combination with a 1,4-dihydroxyaromatic compound. Carbonic acid is similarly suitable.

Among the suitable complementary di-hydroxy compounds are the glycols, such as ethylene glycol and other glycols of formula $HO(CH_2)_nOH$, where n is 2 to 10; cis- and trans-p-hexahydroxylylene glycol; diethylene glycol; quinitol; neopentylene glycol; 1,4-bis-(hydroxyethyl)benzene; and 1,4-bis(hydroxyethoxy)benzene. Other suitable compounds in-

clude dihydroxy aromatic compounds such as 2,2 - bis(4 - hydroxy - 3,5 - dichlorophenyl)-propane, 2,2-bis(4-hydroxyphenyl)propane, hydroquinone, and 2,5- and 2,6-dihydroxy-naphthalene.

The fibres of this invention may also contain suitable light stabilisers, ultraviolet absorbers, delusterants, pigments and dyes. Such agents may be added before, along with, or after the polyether. It is often desirable to add an antioxidant.

The modified polymers (polyesters blended with poly(alkylene ethers) of this invention may be used as components of co-spun yarns in which filaments of two or more different compositions are spun simultaneously to make a mixed filament yarn, either side-by-side or sheath-core relationship. Such a composite yarn bundle may also be separated and given different treatments whereby a differential shrinkage, bulkable yarn is produced, as disclosed, for example, in Specification No. 787157. The modified polymers are also suitable for the process of Specification No. 839418.

The fibres may be used or produced in any state of aggregation, e.g. as plexifilaments, short staple fibres, flock, continuous filaments and staple fibre yarns, tow, cord and fabric.

The fibres may be used, before or after an extraction step, to produce any type of fabric, whether knitted, felted or woven. They are suitable as bristles up to 125 mils in diameter for brushes and brooms. They may be used alone, or may be plied or blended with other fibres, natural, artificial or synthetic. They are readily readily dyed, bleached, pigmented, printed or otherwise coloured. They may be textured, bulked, heat-set, twisted, crimped, or subjected to any combination of these processes. Thus they may be subjected to steam bulking, or to hot air bulking as described in Specification No. 905,895. They may be knitted to tricot, jersey, tissue, satinette or circular knit or full-fashioned hose. They may be woven, alone or in combination with other fibres, to taffeta, twill, satin, sand crepe and the like. The fibres are specially useful in the pile of pile fabrics, such as velvet, plush, rugs, carpets and artificial fur. Rugs and carpets of these fibres are especially useful owing to their antistatic properties, attractive lustre, and fibre opacity combined with an unexpected degree of soil repellence. Their antistatic behaviour is often so effective that a minor proportion serves to reduce to an acceptable level the static propensity of a fabric in which they are combined with unmodified hydrophobic filaments.

The static propensities of fabrics reported below is given in terms of the direct current resistance in ohms per square (the units of area being immaterial), measured parallel to the fabric surface at the given temperature and humidity according to the A/A.T.C.C. method, C-76-59. Numerical values are reported as "log R," which is the logarithm (to the base 10) of the resistance in ohms. High values indicate a tendency to acquire and retain a static charge. Adequate static protection is attained when performance equivalent to cotton is attained; cotton has a log R of 13.1, at 30% RH.

The "wash" used to simulate home laundering is carried out as follows. The fabrics are washed in a tumble-type washing machine with a water temperature of 38°C.; the washed fabrics are given a final spin to extract excess water, followed by tumble drying at 77°C.

By the terms "stable under melt spinning conditions" is meant that the poly(alkylene ether) is neither decomposed nor volatilised during the spinning step.

By the term "microscopic" is meant having a particle size about 0.05 to 2 micron or more in diameter. The length of the polyether particles or "fibrils" is estimated to be from ½ to ten times the fibre diameter. These particles are almost always visible in a light microscope. It is believed that these fibrils are in some way interconnected so that electric charges are conducted away to ground.

The following Examples, in which parts and percentages are by weight unless otherwise specified, illustrate the invention.

EXAMPLE I

Polyethylene terephthalate is polymerised conventionally by reacting dimethyl terephthalate with ethylene glycol. When the evolution of methanol is complete, the reaction product is transferred to an autoclave and the vacuum cycle is begun. Glycol is evolved as high molecular weight polymer is formed. Midway in the polymerisation cycle, a mono-nonylphenyl polyethylene glycol of molecular weight 4600 is added in a glycol slurry. Polymerisation is continued until polymer of spinnable molecular weight is produced. Following the polymerisation, the polymer is extruded as ribbon, cut to flake and then spun to yarn using a screw-melter. The spun yarn samples representative of the test yarn and an unmodified control A are given five washing cycles, each of which is followed by hand ironing at the temperature setting customary for synthetic fabrics. Following the five wash-press cycles, each sample is subjectively rated for static against the unmodified polyester control A at 25% relative humidity. The rating scale goes from 1, severe static, up to 5, no static. Cotton, which is acceptable, has a rating of 3 to 4.

TABLE I

Run	Poly(alkylene ether) Average Mol. Wt.	Concen.	Static Rating after 5 Wash 'Press Cycles
A	None	—	1.0
B	4,600	6%	4.6

Examination of the filaments of sample B with a light microscope shows no visible striations, but when examined at high magnification in an electron microscope, minute striations are evident.

EXAMPLE II

(A) 6% of a polyethylene glycol of molecular weight 20,000 and (B) 6% of the dimethyl ether of this polyethylene glycol is incorporated in a polyethylene terephthalate polymer which is spun to yarn, and the yarn drawn and woven to a filling face satin. Representative fabric yarn samples are coded A and B respectively. The static rating after five wash-press cycles is listed in Table 2 along with a similar result for an unmodified control C. Swatches of the fabric are dyed with a dispersed dye and exposed for 40 hours in a Xenotester to determine dye lightfastness. It is noted that there is no fading for the control C, very slight change in shade for the methyl capped polyether product B, and a severe change in shade for the sample of run A. Skeins of these yarns are boiled in dilute sodium hydroxide solution and the rate at which they lose weight is compared to that of control C.

TABLE 2

Run	A	B	C(Control)
Polyether Compound, Mol. Wt.	20,000	20,000	
Amount added	6%	6%	none
Static rating, 5 Wash/Press Cycles	4.2	4.3	1.0
Disperse Dye Lightfastness	Severe change	Slight change	no change
Caustic Sensitivity, % of control	880	100	100

It is noted that sample B shows a caustic sensitivity (rate of weight loss) equivalent to the control, whereas the rate of weight loss for sample A is almost nine times as fast. It is believed that the rapid rate of caustic attack occurs because the polyether glycol has, in part, become a component of the polyethylene terephthalate chain. The polyether compound capped with methyl groups would not be expected to react during polymerisation, and is believed to be present as a polymer blend component only.

EXAMPLE III

Polymer flake of polyethylene terephthalate, free from delusterant, and having an intrinsic viscosity of 0.76 (measured at 27°C. in a solvent of 10 parts by weight phenol to 7 parts 2,4,6, trichorophenol), is mixed by tumbling with 15% of its weight of a polyethylene ether glycol having a molecular weight of 20,000. The mixture is melted in a screw extruder and immediately spun into yarn at a temperature of about 290°C. The yarn is drawn at a draw ratio of 3.55, to produce a yarn having a break elongation of about 25%. The yarn is then twisted seven turns per inch, is twist set, and is woven into a plain weave taffeta of 104 × 72 construction.

The test fabric is divided into a number of swatches for subsequent tests.

A swatch of the test fabric is scoured for one hour at the boil in a 0.5% aqueous solution of a sodium salt of an unsaturated long-chain alcohol sulphate. The surface lustre of the original fabric is retained but its covering power (opacity) is increased so that it is equivalent to that of a similarly constructed fabric from unmodified polymer containing 0.3% titanium dioxide delusterant.

The destiny of the unextracted yarn is 1.350; the scoured yarn has a density of 1.317. This

compares with a value for the unmodified control of 1.373. Based on the observed density change, it is estimated that 10—20% of the polyether glycol initially present has been extracted. After 25 successive scourings in aqueous synthetic detergent, the scoured fabric has a log R value of 13.1. Another swatch is bleached in peroxide, followed by ten scourings; the log R is 12.8. A swatch of the extracted fabric is exposed to five dry cleaning cycles; the log R is 12.6. Another swatch of the scoured fabric is Soxhlet extracted in methylene chloride for 15 hours; the log R is 13.2. A comparable treated control (without polyether modifier) has a log R of 14.8, which is typical of unmodified polyethylene terephthalate.

That the polyether glycol is present in the polyester fibre as a second phase may be seen by photographs of the fibre at about 700X magnification. Faint striations appearing parallel to the fibre length are due to the high molecular weight polyether glycol phase. After scouring, the yarn has even more pronounced striations and these appear to be voids within the fibre. A second sample, differing only in that 5% of the polyether glycol molecular weight 20,000 is employed, shows fewer striations than are seen in the first sample.

When yet another sample is prepared following the above procedures, using, however, 10% of polyether glycol of molecular weight 9,000, the fibre does not show visible striations. Although there is some indication of a two-phase system, since there appear to be globules of the polyether compound in the fibre, this product does not retain its antistatic properties after scouring, having a log R of 13.8.

EXAMPLE IV

The screw-melter blending procedure of Example III is repeated; however, for this test 2 mol. % of the terephthalate component of the polyester is replaced by an equivalent amount of sulphonated isophthalate. The dimethoxy capped polyethylene ether of molecular weight 20,000 is added, 8% by weight, to the flake, and screw melter spun. After five wash-press cycles, fabric from this polymer has a subjective static rating of 4.3.

The test is again repeated, using a terephthalate copolymer in which 10 mol. % of the terephthalate component is replaced by an equivalent amount of hexahydroterephthalate. 5% of the same polyethylene ether is added to the flake before screw melting. Fabric produced from filaments of this composition have satisfactory static properties.

The process of this Example is again repeated, preparing a polymer of p-hexahydroxylylene terephthalate, (65% trans, 35% cis isomer) to which is added 8% of the same polyethylene ether. When tested according to the procedures described above, it is found to have an antistatic rating equivalent to cotton.

EXAMPLE V

Following the melt blending-spinning procedure of the previous Example, taffeta fabrics are prepared from melt blends of 100 parts polyethylene terephthalate and 6 parts of various polyether compounds, whose end groups R, R^1 are as given in Table 3. Using this melt binding technique, less than 10% of the polyether glycol ($R = R^1 = H$) reacts with the polyethylene terephthalate.

The fabrics are evaluated for static rating after 15 "C" wash cycles.

TABLE 3

Polyether			Static Rating After 15 "C" Wash Cycles
R	R^1	Molecular Weight	
nonylphenyl	H	20,000	4.5
nonylphenyl	H	13,500	3.8
phenyl	H	16,000	4.4
nonylphenyl	CH_3	11,000	3.1
phenyl	CH_3	16,000	3.3
CH_3	H	15,000	4.1
CH_3	CH_3	15,000	4.1
H	H	21,000	3.8

WHAT WE CLAIM IS:—

1. Antistatic oriented melt-spun synthetic fibres, comprising a polyester and, uniformly admixed therein as a separate phase, at least 2% by weight of a high molecular weight poly(alkylene ether) said poly(alkylene ether) being substantially non-reactive with and insoluble in the polyester and stable under melt spinning conditions, and distributed throughout the fibre structure in the form of elongated particles having their longest dimension parallel to the fibre axis.

2. Fibres according to claim 1, wherein the poly(alkylene ether) is capped by one or more ether end groups and has at most one hydroxyl end group.

3. Fibres according to claim 1 or 2, wherein the poly(alkylene ether) is a single or doubly capped polyethylene oxide in which the poly-ether portion of the chain has a molecular weight of at least 1300.

4. Fibres according to any one of claims 1—3, wherein the poly(alkylene ether) is present in the fibres in an amount of 3—15% by weight.

5. Fibres according to any one of the preceding claims, wherein the polyester component is wholly or predominantly polyethylene terephthalate.

6. Antistatic fibres according to claim 1 substantially as hereinbefore described, and textile articles containing them.

7. Process for the production of fibres claimed in any one of claims 1—6, which comprises blending the fibre-forming polyester and poly(alkylene ether) to form a uniform mixture, and melt spinning the mixture so obtained.

8. Process according to claim 7, wherein the polyester and poly(alkylene ether) are blended at a temperature above the melting point of the polyester.

9. Process for the production of fibres according to claim 7 substantially as hereinbefore described.

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